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Density functional theory calculations are used to estimate the energy of interstitial oxygen (O_i) release from tin-doped indium oxide (ITO). It is found that in contrast to the current concept, the local arrangement of tin around O_i has only minor effect on the defect clusters nonreducibility. The extraction energy of interstitial oxygen from ITO critically increases simultaneously with the charge carrier concentration. This effect is rationalized as the noticeable change of doubly charged interstitial oxygen deionization energy caused by screening of ion-ion Coulomb interaction by conductive electrons.

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Tin-doped indium oxide (ITO) is a degenerated semiconductor that is one of the most commonly used transparent conducting oxides. Its optical and electrical properties are exploited in expanding variety of transparent electrode applications, including flat-panel displays, electrochromic windows, organic light-emitting diodes, and solar cells [1, 2]. Although the defect structure of pure and tin-doped In_2O_3 is being studied over the past three decades it continues to attract the unrelenting interest of researchers [3–14].

Pure In_2O_3 crystallizes in the cubic bixbyite structure (space group #206, $Ia\bar{3}$) with 80 atoms or 16 formula units per unit cell [15]. The Sn atoms are considered to substitute for In. The difference of valence between In^{3+} and Sn^{4+} results in the donation of a free electron to the crystal lattice. A critical role in the defect chemistry of this material is played by excess or interstitial oxygen accommodated at the vacant sites of anion sublattice. It traps free electrons donated by Sn eliminating the doping effect.

As it had been deduced by Köstlin *et al.*, there exist associated neutral defects of composition $(2Sn\bullet O_i'')^\times$ formed by two tin substituents and one interstitial oxygen [8]. According to this model there are two types of defects that are named as "reducible" and "non-reducible" depending on the ability to create charge carriers under reduction. The loosely bound reducible cluster, with tin dopant in the nonnearest coordination of O_i , dissociates, giving two free electrons. Recently, Warschkow *et al.* performed an extensive survey of defect clusters and proposed that oxygen interstitials become non-reducible when coordinated by three or more tin cations due to defect cluster aggregation at high doping level [9, 10].

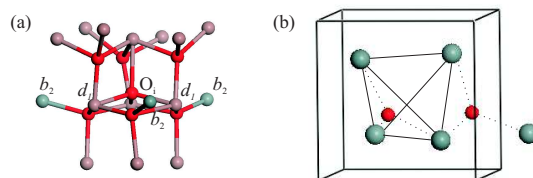
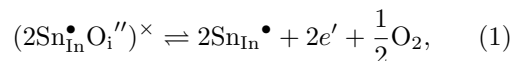


FIG. 1: (a) Local coordination around O_i . All In atoms at b_2 sites are substituted by Sn. (b) Unit cell with two aggregated $(2b_2 \cdot O_i)^\times$ defect clusters. Atoms different from Sn and O_i are hidden. Tin atom in the neighboring unit cell is shown for guidance. All interatomic connections are plotted for the convenience of eyes.

Present investigation is based on periodic density functional theory (DFT) calculations using projector-augmented wave methods with the Perdew-Wang 91 functional implemented in VASP software package. Depending on the relative positioning of structural vacancies, two types of cation sites exist in the unit cell, termed b and d sited in Wyckoff notation. We denote cation positions where Sn substitutes for In by their Wyckoff type (b or d), via a numeric subscript, whether located in the first or second cation coordination shell of interstitial. Kröger-Vink notation is used to describe electrical charge and lattice position for defect species in crystals. To make notation shorter, for each actual configuration of defect both symbols of replaced In atom and Sn substituent are omitted.

The energy E that has to be applied to remove O_i from bulk ITO was calculated as a difference between energies of initial compound and products of following defect dissociation reaction, giving two free electrons:



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TABLE I: Calculated interstitial oxygen release energies for various defect clusters. Calculations performed by using unit cell plotted in Fig. 1b and its derivatives except otherwise denoted.

No.	Initial defect structure	Final defect structure	E (eV)
1	$2(2b_2 \cdot O_i)^\times$	$(2b_2 \cdot O_i)^\times (b_2)^{\bullet\bullet}$	3.28 ^a
2	$(2b_2 \cdot O_i)^\times (2b_2)^{\bullet\bullet}$	$2(2b_2)^{\bullet\bullet}$	4.01 ^a
3	$(2b_2 \cdot O_i)^\times$	$(2b_2)^{\bullet\bullet}$	3.81 ^b
4	$(2d_1 \cdot O_i)^\times$	$(2d_1)^{\bullet\bullet}$	4.08 ^b
5	$2(2b_2 \cdot O_i)^\times$	$(2b_2 \cdot O_i)^\times (2b_2)^{\bullet\bullet}$	4.05
6	$(2b_2 \cdot O_i)^\times (2b_2)^{\bullet\bullet}$	$(2b_2)^{\bullet\bullet}(2b_2)^{\bullet\bullet}$	5.30
7	$(3d_1 \cdot O_i)^\bullet (d_1 \cdot O_i)'$	$(3d_1 \cdot O_i)^\bullet (d_1)^\bullet$	4.23
8	$2(2d_1 \cdot O_i)^\times$	$(2d_1 \cdot O_i)^\times (2d_1)^{\bullet\bullet}$	4.31
9	$(3d_1 \cdot O_i)^\bullet (d_1 \cdot O_i)'$	$(3d_1)^{\bullet\bullet\bullet} (d_1 \cdot O_i)'$	4.50
10	$(3d_1)^{\bullet\bullet\bullet} (d_1 \cdot O_i)'$	$(3d_1)^{\bullet\bullet\bullet} (d_1)^\bullet$	5.37
11	$(2d_1 \cdot O_i)^\times (2d_1)^{\bullet\bullet}$	$(2d_1)^{\bullet\bullet}(2d_1)^{\bullet\bullet}$	5.47
12	$(3d_1 \cdot O_i)^\bullet (d_1)^\bullet$	$(3d_1)^{\bullet\bullet\bullet} (d_1)^\bullet$	5.64
13	$(3b_2 \cdot O_i)^\bullet$	$(3b_2)^{\bullet\bullet\bullet}$	4.84
14	$(3d_1 \cdot O_i)^\bullet$	$(3d_1)^{\bullet\bullet\bullet}$	5.19

^aCalculated by using $2 \times 1 \times 1$ supercell.

^bCalculated by using single unit cell with non-aggregated defect cluster.

Calculation results for various defect structures are summarized in Table I.

At first, a supercell constructed from two ITO's unit cells, each containing one defect cluster with two Sn dopants at b_2 sites was considered. All the defects in this supercell are nonaggregated. Corresponding to the current concept, the defect energy has to be driven only by the local coordination of Sn around the interstitial oxygens and should not depend on any other parameter. In contrast, we had found that the O_i release energy critically depends on the actual oxidation state of ITO. The energy that should be applied to remove the first of two interstitials is estimated to be 3.28 eV, while the same value for the second residual interstitial is 4.01 eV.

The aggregated defect cluster that is expected

to possess a constant value of E is presented in Fig. 1b. It consists of two $(2b_2 \cdot O_i)^\times$ clusters and each of O_i is equivalently coordinated by tin. Four Sn cations form a tetrahedra with length of edge equal to 0.73 nm. Each O_i is coordinated by three Sn. In contrary to expectations, E also crucially depends on the oxidation state of ITO. It is necessary to apply the energies of 4.05 and 5.30 eV to remove the first and second interstitial oxygen one after another (processes 5 and 6 in Table I).

To study the effect of local stoichiometry relatively to the conductive state, a number of derivatives from the structure in Fig. 1b were constructed to make the interstitial oxygens be coordinated by one, two or three tin atoms at d_1 sites (reduction processes No. 7–12 in Table I). Dopant atoms are placed at the first coordination shell to avoid an aggregation with neighboring defect clusters.

As it is seen from results in Table I, there are two causes for the E value variation. The first one is the well-known effect of local coordination that is evident from comparison of processes 7 against 9 and 10 against 12. The second and most important source of E value variation is the oxidation level of both initial and final states during the reduction process. It can be deduced from the comparison of energies that have to be applied to release equivalently coordinated O_i . The pairs of such processes are 7 and 10, 8 and 11, and 9 and 12.

The revealed effect imposes a limitation on the reduction of ITO. This restriction weakly depends on the local coordinartion of the interstitial oxygen by tin dopants. It is mainly formed by the relation of doubly charged oxygen anion deionization energy to the free electron density. The more detailed consideration of discussed phenomena will be published soon.

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